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X-RAY DIFFRACTION STUDIES OF THE HYDRIDES OF ZIRCONIUM, TITANIUM, AND HAFNIUM AT ELEVATED TEMPERATURES

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ABSTRACT

X-ray diffraction data have been obtained for the hydrides of titanium, zirconium, and hafnium from room temperature to 650°C and at hydrogen gas pressures from 2 mm. to 600 psi. No new hydride phases were observed. Evidence has been obtained in support of the work of Vaughan that the various phases previously reported for zirconium hydride, are derived from the tetragonal phase with the axial ratio, c/a, less than one. When hydrogen is slowly removed from ϵ - ZrH_2 ($c/a < 1$), the axial ratio. increases to and may pass through unity. Hafnium hydride transforms from a tetragonal to the cubic phase in the same manner as does zirconium hydride. The lattice parameter of cubic hafnium hydride ranges from 4.722-4.719Å, and from 4.717-4.714 A; the parameters are both temperature and pressure dependent. The only hydride phase observed for titanium hydride is the face-centered cubic phase. The anomalous variation of lattice parameter of titanium hydride with temperature at constant pressure may be attributed to a change of some of the hydrogen positions from the tetrahedral sites to the octahedral sites of a fluorite type lattice.

I. INTRODUCTION

Titanium, zirconium, and hafnium are representative of a class of metals known as "exothermic occluders" of hydrogen. The fully hydrided metals undergo a volume expansion of approximately 15% over that of the metal lattices. The composition of the non-stoichiometric hydride is both temperature and hydrogen pressure dependent.

Hägg (1) was the first to study the titanium-hydrogen system by means of X-ray diffraction. His investigation showed only one hydride phase in addition to the metal phase. The structure of the hydride phase, which existed between 50 to 66 atomic per cent hydrogen, was face-centered cubic. Using X-ray and neutron diffraction, Sidhu (2) and his coworkers reported observing one hydride phase in addition to the metal phase, and the possibility of a tetragonal structure at compositions very close to stoichiometric TiH_2. Both Hägg and Sidhu performed their diffraction studies at room temperature.

The first X-ray studies of the zirconium-hydrogen system were carried out by Hägg (3). Four hydride phases were reported; however, the studies were performed on quenched specimens. Only two hydride phases were confirmed by Gulbransen and Andrew (4) by means of X-ray diffraction and dissociation pressure studies. Vaughan and Bridge (5) have obtained X-ray diffraction data on zirconium hydride at elevated temperatures with specimens contained in evacuated silica capsules. Their results led them to believe that there is only one hydride of zirconium, which goes through a succession of "degrees of tetragonality" with varying composition.

A structural study of the hafnium-hydrogen system has been made by Sidhu and his coworkers (6, 7, and 8). The results indicate the existence of several hydride phases in addition to the metal phase. A deformed cubic phase extends up to $HfH_{1.53}$ and converts to a face-centered cubic phase at approximately $HfH_{1.55}$. Transformation to a tetragonal phase occurs at about $HfH_{1.80}$.

With the exception of the studies of the $Zr-H_2$ system by Vaughan and Bridge[*], X-ray diffraction studies on the group IV-A metal hydrides have been limited to room temperature investigations on rapidly cooled samples prepared at elevated temperatures. It has become increasingly apparent that any X-ray diffraction investigation of the true structures of the hydride phases as they exist at elevated temperatures in any one system should be performed at elevated temperatures in a hydrogen atmosphere. In this research, X-ray diffraction studies were performed at temperatures from room temperature to 750°C and hydrogen pressures from 1 mm. to 600 psi hydrogen. In addition to gathering diffraction data under these conditions, the structural behavior of the hydrides under varying temperatures and pressures has been studied.

[*] Recent article "Thermocrystallography of Higher Hydrides of Titanium and Zirconium," H.L. Yakel, Jr., Acta Cryst. 11, 46(1958).

II. X-RAY DIFFRACTION EXPERIMENTS

A. Apparatus

Powder diffraction patterns were obtained with a General Electric XRD-4 diffraction unit using copper radiation. The specimen holder, temperature control assembly, apparatus for containing and measuring hydrogen gas pressures, and method for measuring specimen temperature have been described in a paper published in the *Review of Scientific Instruments* (9).

The resistance furnace has been modified to allow operation at higher temperatures and to surround the specimen holder with an atmosphere of helium. As seen in Figure 1, the heating element is encased in a vycor sleeve to prevent expansion of the coils in the X-ray beam. An inlet, made of 1/8" O.D. copper tubing, allows an inert gas like helium to flow into the furnace. The latter step is necessary because of the increase in reaction rate of beryllium with oxygen and nitrogen gases at temperatures in excess of 600°C.

The electronic apparatus, which was used to maintain essentially a constant specimen temperature in the beryllium capillary and the method used to determine the specimen temperature have been described in a previous report NYO-7545 (10).

B. Materials

a) *Hydrogen.* The hydrogen used in the preparation of our hydride specimens was purified as follows. The commercially available hydrogen was passed through a Deoxo purifier to remove traces of oxygen, a column of Drierite, and finally through a bed of hot uranium.

b) *Specimens.* All metals were of high purity. Three types of titanium metal were used: sodium reduced titanium crystals obtained from National Distillers; sheet metal from the Alloy Division of the National Lead Company; and drip melt metal from Nuclear Metals, Inc. Nuclear grade crystal bar zirconium with less than 0.1% hafnium was obtained from Westinghouse Electric Corp. Hafnium crystal bar was a product of the National Research Corp.

C. Preparation of Hydrides

a) *Preparation of Metals.* Two samples of each metal were prepared for each hydriding run. The larger piece was later used for X-ray studies. The smaller sample, which was placed in front of the large sample in the vycor hydriding tube, acted as a getter for any traces of impurities which may still be in the hydrogen. Although the size and weight of the samples varied for different metals, all were prepared and hydrided in the same manner. The samples were first etched in a solution of 5% HF, 45% concentration HNO_3, and 50% distilled water. All etchings were carried out in polyethylene

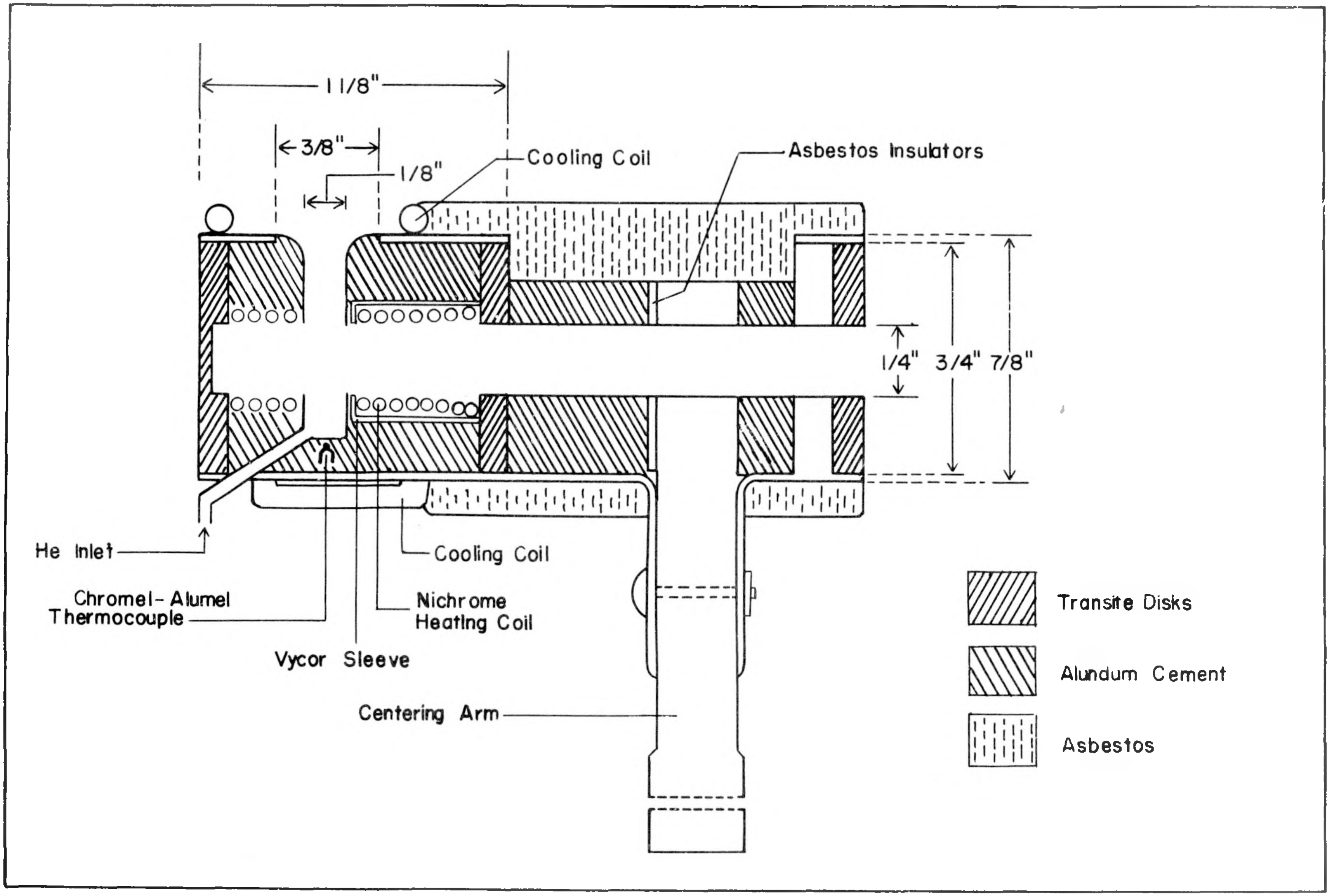

FIGURE 1. RESISTANCE FURNACE

ware until the metal surfaces were lustrous. This was usually complete in 30 to 60 seconds. Subsequent washings in distilled water, isopropyl alcohol, and anhydrous ether followed. The samples were then quickly weighed in air. They were then re-etched in a fresh solution of hydrogen fluoride for five seconds, and washed as before. The second etching solution was saved for analysis for metal, and the initial weight of metal corrected. The samples were left under ether prior to pumping off the ether in the dry box air-lock and subsequent loading into the vycor specimen tube in an argon filled dry box.

b) Boats. Stainless steel boats were used to contain the samples to prevent a reaction between the metal specimen and vycor tube at elevated temperatures. These were prepared from sheets of stainless steel, and were washed in acetone, 5:1 hydrochloric acid solution, distilled water, and ether.

c) Hydriding. The specimen was heated until the first sign of hydrogen pick-up occurred. Then the temperature was increased another 100° and kept constant until absorption ceased. The composition of the hydride was calculated from pressure-volume-temperature relationships, and confirmed by chemical analysis.

III. RESULTS

A. Zirconium Hydride

Two samples of zirconium hydride of the compositions, $ZrH_{1.95}$ and $ZrH_{2.02}$, were prepared. It is doubtful that greater than stoichiometric ZrH_2 was actually obtained. X-ray patterns of both samples contained lines of equal intensity and resolution. In Table I are listed the d-spacings for the hydride lines of ϵ - zirconium hydride taken through glass and beryllium capillaries and the corresponding values as found in the ASTM card files (11). The d-spacings were assigned Miller indices with the aid of Bunn charts. Lattice constants a_o and c_o were calculated from the equation for a tetragonal structure. The parameter values obtained through glass were: $a_o = 4.980$ Å, $c_o = 4.445$ Å, and $c_o/a_o = 0.893$; those through beryllium, $a_o = 4.976$ Å, $c_o = 4.448$ Å, $c_o/a_o = 0.894$. The precision of the measurements was ± 0.001 Å. These values agreed quite well with values reported by Hägg (1).

The effect of pressure and temperature on the hydride lattice was studied by subjecting the zirconium hydride to hydrogen pressures of one atmosphere, 350 psi, and 550 psi. The results are tabulated in Table II. The change of c_o and a_o with temperature is shown in Figure 6 and the variation of the axial ratio with temperature is plotted in Figure 7. The results of Vaughan and Bridge (5) are also included in Figure 7.

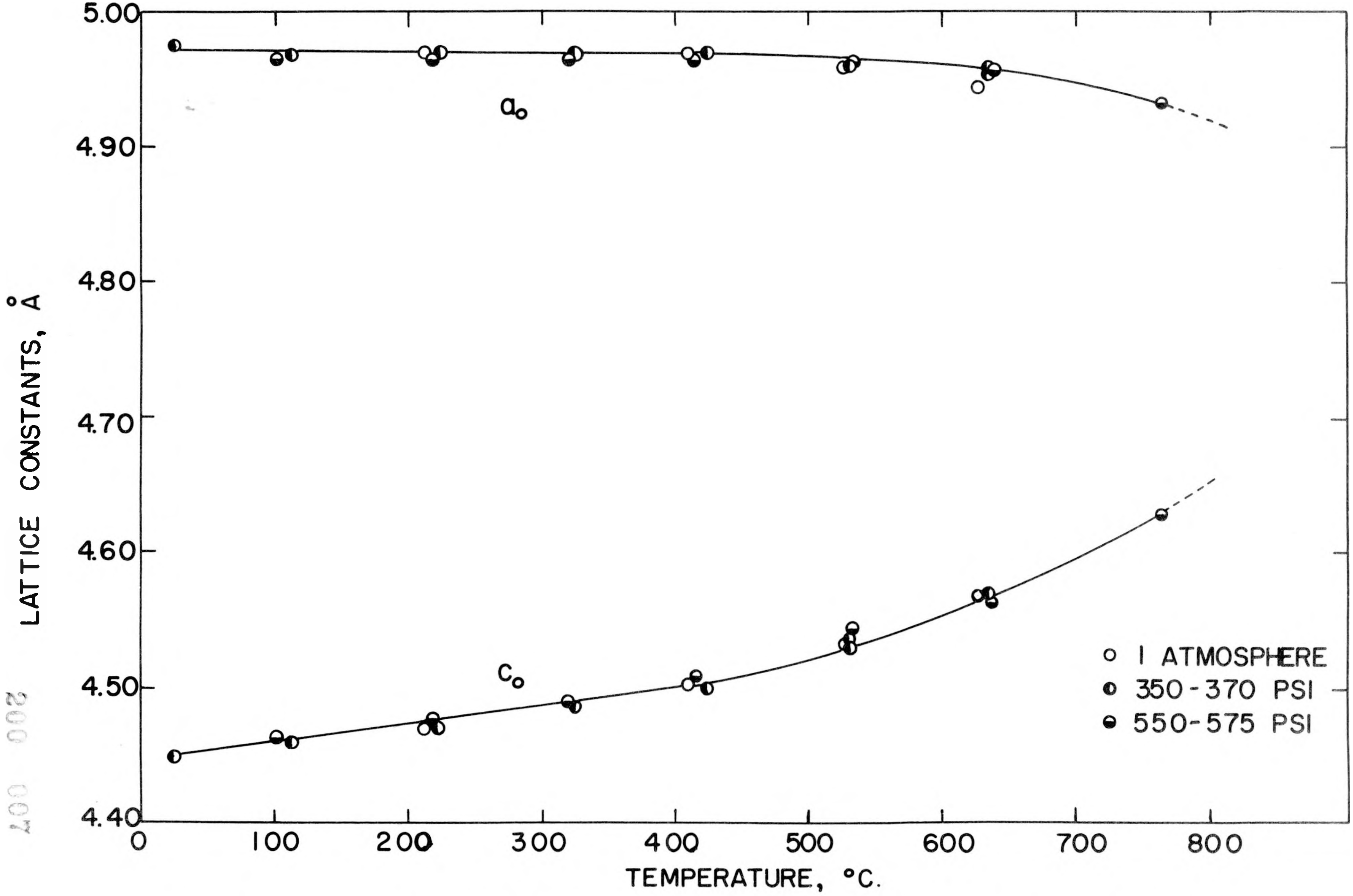

FIGURE 6. LATTICE CONSTANTS OF ϵ-ZrH_2 vs TEMPERATURE

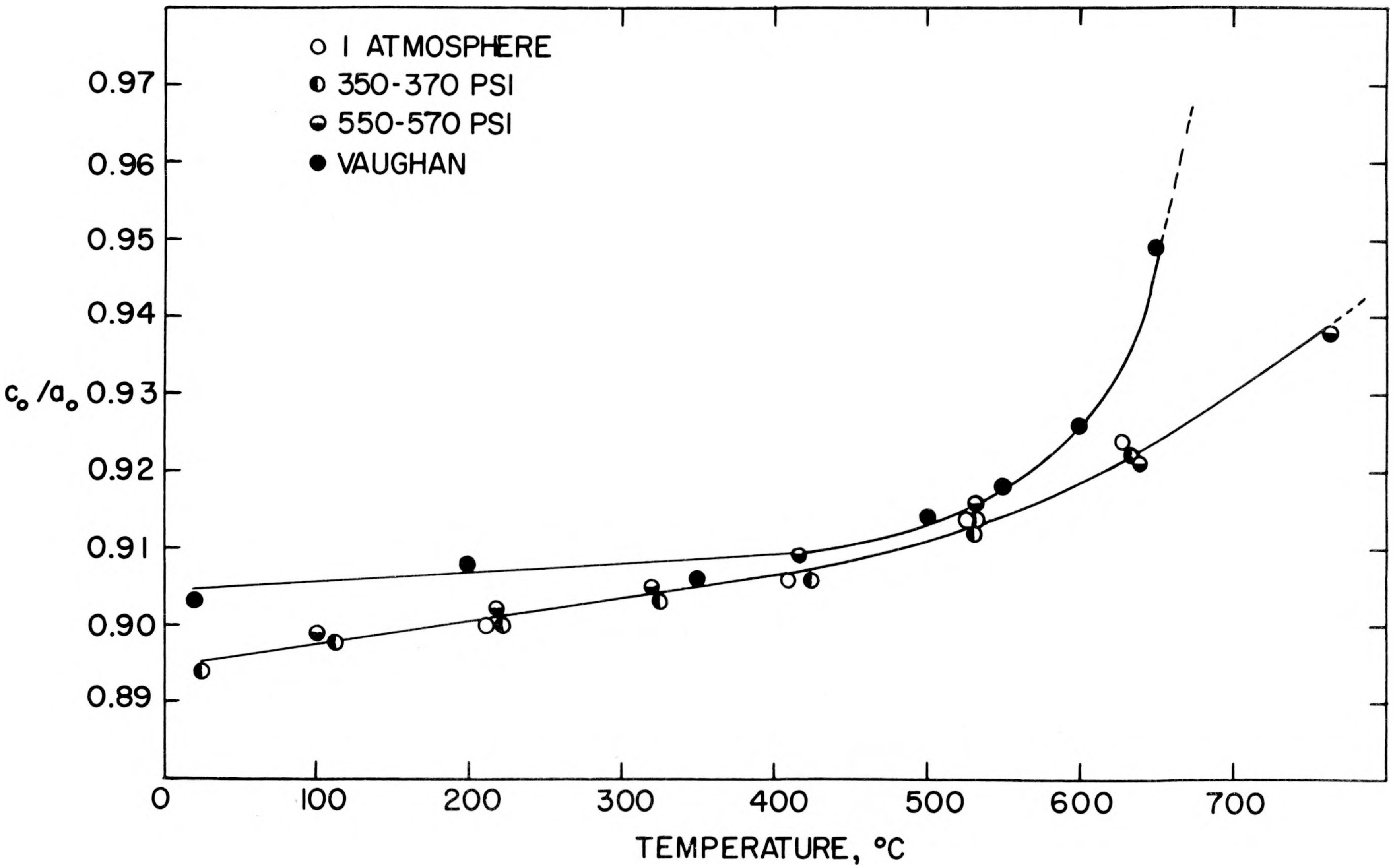

FIGURE 7. AXIAL RATIO CHANGE OF ϵ-ZrH_2 WITH TEMPERATURE

TABLE I

d-SPACINGS FOR TETRAGONAL ε-ZrH_2 AT ROOM TEMPERATURE

hkl	d (obs.) through glass	d (ASTM)	d (obs.) through Be
424	0.7869	-	0.7865
513	0.8157	-	masked
442	0.8187	-	masked
404	0.8296	-	0.8291
531	0.8392	-	0.8380
441	0.8629	-	0.8625
440	0.8819	-	0.8802
304	0.918	-	0.919
-	0.937	-	masked
-	0.950	-	masked
422	0.992	0.995	masked
204	1.01	1.02	masked
313	1.075	1.08	1.053
402	1.080	1.09	masked
420	1.110	1.11	1.106
331	1.132	1.13	masked
400	1.240	1.24	1.236
113	1.360	1.37	masked
222	1.375	1.38	1.379
311	1.475	1.48	1.476
202	1.65	1.66	1.65
220	1.75	1.76	masked
002	2.20	2.22	2.22
200	2.47	2.49	2.47
111	2.74	2.76	2.76

TABLE II

LATTICE CONSTANTS OF ϵ-ZrH_2 WITH VARYING PRESSURE AND TEMPERATURE

1 Atmosphere				350-370 PSI				550-575 PSI			
Temp.	a_o, Å	c_o, Å	c_o/a_o	Temp.	a_o, Å	c_o, Å	c_o/a_o	Temp.	a_o, Å	c_o, Å	c_o/a_o
				R.T.	4.976	4.448	0.894				
				113°C	4.969	4.461	0.898	102°C	4.967	4.465	0.899
212°C	4.973	4.473	0.899	223	4.972	4.472	0.899	218	4.966	4.478	0.902
				326	4.971	4.488	0.903	320	4.965	4.492	0.905
410	4.970	4.503	0.906	424	4.970	4.501	0.906	416	4.965	4.511	0.909
527	4.961	4.534	0.914	532	4.966	4.530	0.912	533	4.964	4.545	0.916
				532	4.965	4.537	0.914				
626	4.946	4.568	0.924	635	4.956	4.579	0.924	638	4.958	4.564	0.921
								640	4.959	4.566	0.921
								765	4.933	4.628	0.938

All diffraction patterns from room temperature to 500°C contained sharp, well resolved lines in the back reflection region. The diffraction lines were noticeably more diffuse at 635°C, and runs between 700°-800° generally produced no high angle lines. The sole exception to this was a run made at 765°C and 571 psi of hydrogen gas, which produced back reflection diffraction lines of sufficient resolution and intensity to be read.

At temperatures above 750°, there were no lines present in the low angle region, which could be attributed to zirconium hydride. There was a distinct possibility of the formation of a Zr-Be intermetallic compound at these elevated temperatures. This was confirmed by direct analogy to Mason's (12) X-ray studies of UBe_{13}. The low angle lines could not be attributed to the formation of ZrO or ZrN.

B. Hafnium Hydride

Two samples of hafnium hydride of composition $HfH_{1.90}$ and $HfH_{1.93}$ were prepared. In Table III are listed d-spacings of the tetragonal hydride taken through glass at room temperature and the values obtained by Sidhu (6). The lattice constants, which were calculated in the same manner as for zirconium hydride, were as follows: $a_o = 4.906 \pm 0.005$ Å, $c_o = 4.362 \pm 0.005$ Å , and $c_o/a_o = 0.889$. There is some discrepancy between these values and those obtained by Sidhu. However, Sidhu's values could not be reproduced using his reported data.

The diffraction patterns of tetragonal hafnium hydride through glass or beryllium showed diffuse, non-resolved lines in the back reflection region. Lack of resolution of high angle diffraction lines at elevated temperatures made it impossible to obtain lattice parameter values for any tetragonal hafnium hydride taken through the beryllium capillary.

Cubic hafnium hydride, which is face-centered, gave well resolved back reflection lines. The diffraction lines 600 and 531 were used in all lattice parameter calculations. Since no dissociation pressure measurements are available for the Hf-H_2 system, the effect of varying the pressure of hydrogen gas over the cubic hydride was studied isothermally. The temperature, at which the experiments were run, were 407°, 506°, and 591°C. The data are tabulated in Table IV and plotted in Figure 8. The data show that at constant pressures less than one atmosphere, the lattice parameter of cubic hafnium hydride decreases with increasing temperature. It was observed that when the pressure of hydrogen gas over the sample, which was maintained at constant temperature, was increased, the lattice parameter increased. At pressures greater than one atmosphere, there are regions along the isotherms where the lattice parameter remains constant.

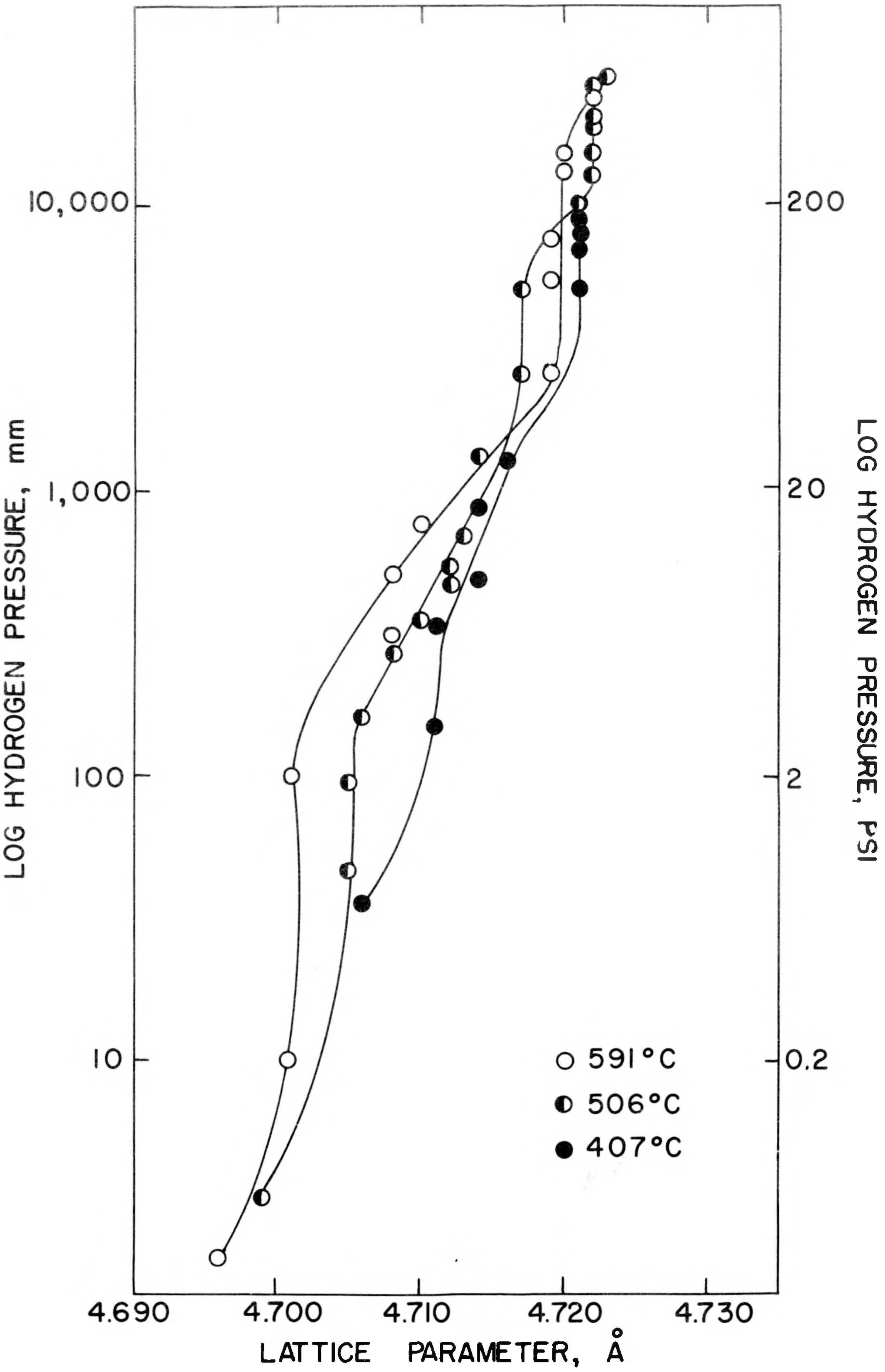

FIGURE 8. LATTICE PARAMETER OF CUBIC HAFNIUM HYDRIDE vs PRESSURE

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TABLE III

d-SPACINGS FOR TETRAGONAL $HfH_{1.93}$ LINES AT ROOM TEMPERATURE

hkl	d (obs.) through glass	d (Sidhu)
111	2.70	2.71
200	2.43	2.44
002	2.17	2.197
220	1.73	1.727
202	1.62	1.631
311	1.455	1.455
222	---	1.356
113	1.334	1.348
400	1.224	1.219
331	1.115	1.113
420	1.095	1.091
313	1.063	1.064
204	0.995	1.002
422	0.977	0.977
511	0.938	0.935
224	0.922	0.928
333	0.905	0.905
440	0.867	0.863
115	0.856	0.853
531	0.826	0.822
404	0.815	0.817
442	0.805	0.802

TABLE IV

THE EFFECT OF HYDROGEN PRESSURE ON CUBIC HAFNIUM HYDRIDE*

407° Isotherm Pressure	a_o	506° Isotherm Pressure	a_o	591° Isotherm Pressure	a_o
		540 psi	4.723 Å		
500 psi		500	4.722		
		490	4.722	493 psi	4.722 Å
		400	4.722		
		400	4.722		
Tetragonal		350	4.722		
		300	4.722	300	4.720
		250	4.722		
		200	4.721	200	4.720
180					
175	4.721 Å**				
160	4.721**				
				150	4.719
140	4.721			107	4.719
100	4.721	100	4.717	100	4.717
		50	4.717	50	4.719
25	4.716	26	4.714		
17	4.714			15	4.710
		692 mm	4.713		
		545	4.712	516 mm	4.708
478 mm	4.714	465	4.712		
343	4.711	358	4.710	314	4.708
		268	4.708		
152	4.711	162	4.706		
		95	4.705	102	4.701
36	4.706	47	4.705		
		3.3	4.699**	10	4.701**

*Accuracy of lattice parameter measurements is ± 0.001 Å.

**Accuracy of lattice parameter measurements is ± 0.005 Å.

The tetragonal hafnium hydride was never observed at 506° or 591°C even when the hydrogen gas pressure was raised to 540 psi. However, at 407°C, the tetragonal phase exists at pressures of 180 psi or greater. The transformation of phases occurred in the pressure range from 180 psi to 140 psi.

The temperature range was determined at which the transformation from the cubic to the tetragonal phase at one atmosphere hydrogen occurred, and was found to be from 360° to 370°C.

C. Titanium Hydride

Four hydride samples were prepared, and their compositions are listed in Table V.

TABLE V

Composition of Titanium Hydride Samples

Composition: P-V-T Data	Composition Combustion Analyses
$TiH_{1.96}$	*
$TiH_{1.94}$	*
$TiH_{1.96}$	$TiH_{1.97}$
$TiH_{2.02}$	$TiH_{1.98}$

*Combustion analyses not run.

Neither the type of titanium metal used (see Specimens Section, page 2) nor the number of times hydrogen was desorbed and reabsorbed by the metal had any effect on the quality of the diffraction patterns. The hydride lines were weak and not resolved in the back reflection region. A comparison of the cubic hydride lines obtained at room temperature with the values obtained by Sidhu (2) are shown in Table VI.

TABLE VI

d-SPACINGS OF CUBIC TITANIUM HYDRIDE AT ROOM TEMPERATURE

hkl	d, (obs.) through glass	d, (Sidhu)
111	2.560	2.563
200	2.220	2.221
220	1.568	1.569
311	1.340	1.339
222	1.284	1.281
400	1.115	1.112
331	1.021	1.019
420	0.996	0.993
422	0.908	0.906
333,511	0.857	0.854

A lattice parameter of a_o = 4.450 ± 0.005 Å is the most consistent value obtained from the diffraction patterns of the$_o$samples listed in Table V. Sidhu reports a value of 4.440 ± 0.003 Å.

A series of runs were made at three different pressures 100, 280, and 450 psi through a temperature range from room temperature to 600 . Results are tabulated in Table VII.

TABLE VII

VARIATION IN LATTICE PARAMETER OF CUBIC TITANIUM HYDRIDE WITH TEMPERATURE AND PRESSURE

100 - 102 psi		275 - 280 psi		430 - 440 psi	
Temperature	a_o	Temperature	a_o	Temperature	a_o
R.T.	4.442 Å	R.T.	4.437 Å	R.T.	4.437 Å
128°C	4.446	128°C	4.442	112°C	4.439
280	4.459	272	4.451	259	4.446
		403	4.460	355	4.448
506	4.455	504	4.458	468	4.456
627	4.448	622	4.450	567	4.452
				591	4.452
				600	4.447

Since the diffraction lines from which the lattice parameters were calculated showed only slight resolution at best, the accuracy of the parameters was only good to ± 0.003 Å. Only the 511 and 422 lines were of sufficient intensity to be used for parameter measurements. These results are plotted in Figure 9. It is believed that the variation in parameter values at room temperature with different hydrogen pressures is due mainly to the history of the sample prior to taking the diffraction patterns.

Parameter measurements for cubic titanium hydride at 600°C from 15 psi to 570 psi were made to substantiate the results plotted in Figure 9. The parameter a_o ranged from 4.434 Å at 15 psi to 4.459 Å at 570 psi. It should be noted that at constant temperature, a_o increases with increasing hydrogen pressure over the hydride.

IV. DISCUSSION

A. Zirconium Hydride.

Within the range of temperatures and pressures used in this investigation, only one hydride of zirconium was encountered. This was the face-centered tetragonal phase (ϵ-ZrH_2 with $c/a < 1$) described by Hägg in his X-ray studies at room temperature. The tetragonal structure undergoes an anisotropic expansion with temperature as shown in Figure 6. From room temperature to 450°C, a_o remains essentially constant while c_o increases linearly. Above 450°C, a_o begins to decrease while c_o starts to increase at a faster rate. Data obtained by Yakel (13) on specimens of $ZrH_{1.92}$ under a pressure of one-third atmosphere hydrogen at temperatures up to 500°C are in excellent agreement with our own. The axial ratio, c_o/a_o, increases at a faster rate above 450°C than below the latter temperature. It is interesting to note that initial hydrogen absorption by the metal occurs around 450° to 500°C. Also partial dissociation of a fully hydrided sample occurs between 425° to 450°C.

At temperatures up to 450°C, pressures from one atmosphere to 550 psi have little effect on the variation of axial ratio. Data indicate that above 450°C, there may possibly be an effect of pressure on the hydride lattice, however, this could not be definitely determined due to experimental difficulties. It will be shown below that the change in axial ratio is the result of the anisotropic expansion of the lattice with temperature accompanied by a decrease in hydrogen content of the hydride. Previous workers (3,4, & 5) have shown that at constant temperature, there is an increase in c_o/a_o with decreasing hydrogen content.

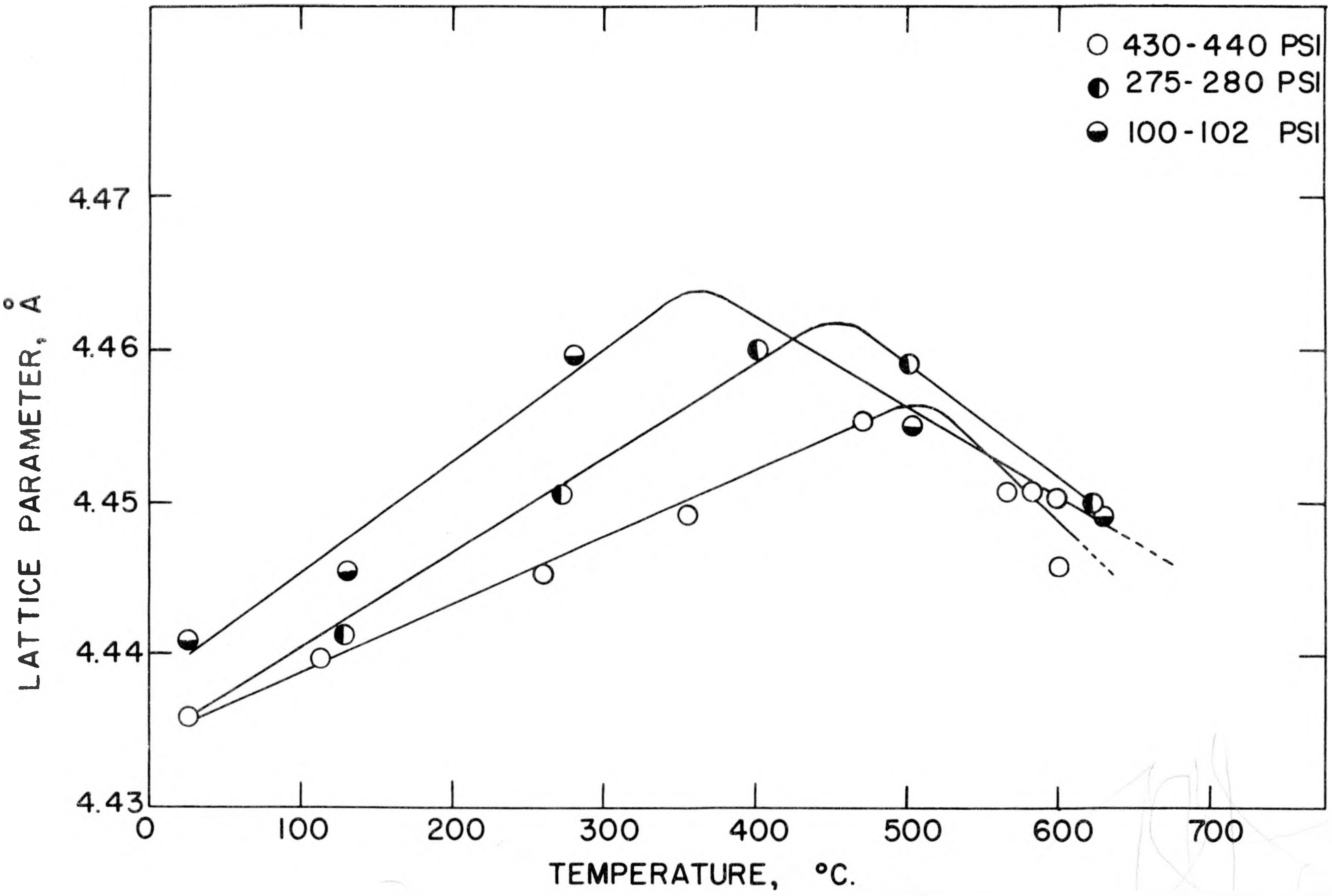

FIGURE 9. LATTICE PARAMETER OF TITANIUM HYDRIDE vs TEMPERATURE

The Bunn chart for the tetragonal structure was used in the interpretation of the powder diffraction patterns. The chart is a plot of logarithm of the axial ratio versus the logarithm of d-spacings and shows for all values of the Miller indices, hkl, the relationship between c_o/a_o and d-spacings. If one follows the traces of the 424, 404, and 531 lines on the chart from small values of c_o/a_o to larger values, one observes that the 424 line shifts slightly to smaller d-values, the 404 line does not shift, and the 531 line shifts to smaller d-values at a faster rate than the 424 line. On the other hand, thermal expansion should cause all the lines to shift to larger d-values. Examination of the diffraction patterns taken at elevated temperatures shows that both the 424 and 404 lines shifted to larger d-values due to thermal expansion. However, the 531 line first remained constant, and then began to shift to smaller d-values at temperatures greater than 500°C. The lack of movement of the 531 line on the pattern taken at temperatures less than 500°C may be interpreted as a cancellation of the effect of thermal expansion by dissociation of the hydride. The dissociation results in a loss of hydrogen from the hydride lattice and in the formation of hydrogen vacancies. At temperatures greater than 500°C, the effect of dissociation is greater than the effect of thermal expansion with the resulting shift of the 531 line to smaller d-values. Therefore, the axial ratio does increase as the hydrogen content decreases. Also the high external gas pressures were sufficient only to partially suppress the dissociation of the hydride.

Extrapolation of Vaughan's data (Figure 7) indicates that sufficient dissociation would occur between 700° and 800°C to obtain the δ-hydride with c_o/a_o equal to unity. This corresponds to Hägg's cubic hydride of composition $ZrH_{1.5}$ and a_o equal to 4.778 Å. It can also be seen from Figure 7 that Vaughan's rate of change of axial ratio between 550° and 650°C is much faster than indicated in our study. Our results indicate that an external hydrogen gas pressure over the hydride at temperatures in excess of 500°C prevents dissociation of the hydride at the temperature observed by Vaughan. Vaughan's diffraction studies were conducted on samples contained in evacuated silica capsules. Therefore, before equilibrium pressures were reached, the amount of hydrogen evolved from his samples was greater than from our samples. Hydrogen pressures greater than one atmosphere may suppress but cannot prevent dissociation of hydride.

It cannot be predicted whether at elevated temperature c_o would eventually become equal to a_o at pressures greater than one atmosphere. The high temperature needed to bring about dissociation of the hydride against this external gas pressure may necessitate exceeding the temperature for the α to β transformation of zirconium metal (840-870°C). Hall et al (14) have shown that at 825°C, zirconium metal absorbs a greater amount of hydrogen than at 800°C. Therefore, the continuity of the curve of the plot of c_o/a_o vs. temperature would be undoubtedly terminate at the transition point of zirconium.

Vaughan found that the axial ratio of a sample of 55 atomic per cent hydrogen was greater than unity at room temperature. It is speculative whether the axial ratio of zirconium hydride at elevated temperature and pressure would become greater than unity. If one refers to the X-ray diffraction study on titanium deuteride by Yakel (13), and draws an analogy between zirconium and titanium, one would not expect to find the axial ratio, c_o/a_o, greater than unity. c_o would approach a_o with increasing temperature; once the hydride had transformed to the cubic structure, it would remain cubic even at higher temperatures.

It now appears that the four phases found by Hägg, two of which were confirmed by Gulbransen and Andrew, are in reality derived from a face-centered tetragonal phase with c_o/a_o less than one. The tetragonal phase, on losing hydrogen gradually, transforms to the cubic phase. Possibly, the cubic phase transforms to another tetragonal phase with c_o/a_o greater than one on further loss of hydrogen. The existence of the various phases previously reported for zirconium hydride have been confirmed, and the structural relationship among the phases has now been clearly demonstrated.

B. Hafnium Hydride.

Both the cubic and tetragonal phases reported by Sidhu were observed in this research. It was expected that the transformation of hafnium hydride from the tetragonal to the cubic phase would occur in the same manner as for zirconium hydride. Unfortunately, lack of resolution of the diffraction lines from the tetragonal hydride prevented determination of lattice parameters. It was inferred from the following observation that the phase transformation for hafnium hydride is analogous to that of zirconium hydride. ϵ-zirconium hydride with c_o equal to 4.447 Å and a_o equal to 4.978 Å (FCT) undergoes an anisotropic change to the cubic structure with a_o equal to 4.778 Å. This involves a 4% contraction of a_o and a 7% expansion of c_o. The a_o and c_o of tetragonal hafnium hydride undergo identical percentage changes on forming the cubic structure.

The complex dependence of cubic hafnium hydride on temperature and pressure is shown in Figure 8. It is interesting to note that at pressures less than two atmospheres, the lattice parameter decreases with increasing temperature. This effect resembles the decrease in parameter of titanium hydride with increasing temperature beyond the maximum of the curves shown in Figure 9. A possible explanation will be given in the Titanium Hydride section.

It was also noted that at constant temperature, a decrease in hydrogen pressure over the hydride results in a decrease of the lattice parameter. If one assumes that the number of hydrogen vacancies in a hydride lattice increases with a decrease in hydrogen pressure over the hydride, then one would have expected the parameter for cubic hafnium hydride to either remain constant or decrease. At the present time, the observed effect can not be explained.

From Figure 8, the lattice parameter of cubic hafnium hydride at 591°C increases to a greater value than that measured at 506°C at hydrogen pressures between 50 to 180 psi. If the hydrogen pressures are increased above 180 psi, then once again the parameters measured at 506°C are greater than those measured at 591°C. The change in parameter may be due to a shift in the positions of the hydrogens. Dissociation pressure studies at high pressures may confirm the parameter changes of cubic hafnium hydride observed by X-ray diffraction.

The data in Table IV indicate that cubic hafnium hydride may exist as two cubic structures both dependent upon temperature and pressure. One cubic structure has a_o varying from 4.719 to 4.722 Å, while the other cubic structure has a_o varying from 4.714 to 4.717 Å. Although the parameters appear to fall into two ranges, it cannot be said with certainty that two separate cubic hydride phases exist. Further speculation on this matter will be postponed until data from dissociation pressure studies are available.

C. Titanium Hydride.

The only titanium hydride phase observed in this research was the face-centered cubic fluorite structure first reported by Hägg. Neutron diffraction studies by Sidhu et al (2) indicate that the hydrogens are in the tetrahedral holes of the fluorite structure. We did not observe the face-centered tetragonal phase, which was studied by Yakel at low temperatures (< 37°C). No evidence was found for Gibb's novel γ-phase. However, the pressure apparatus used in conjunction with the X-ray diffraction assembly was capable of producing only the lower limiting conditions for the γ-phase (500°C, 650 psi).

At constant pressure, the lattice parameter of cubic titanium hydride increases linearly with temperature, reaches a maximum, and then decreases with increasing temperature (Figure 9). The initial increase in parameter with temperature appears to be normal thermal expansion. In the region of normal thermal expansion, the lattice parameter is evidently dependent upon the external hydrogen pressure over the hydride (which governs the hydrogen content of the phase). At room temperature and a pressure of one atmosphere hydrogen, the parameter is 4.450 ± 0.005 Å. Yakel (13) recently reported 4.454 Å at 42°C. At pressures of 100 psi, 280 psi, and 440 psi, the parameters are 4.442 Å, 4.437 Å, and 4.437 ± 0.003 Å respectively. The contraction of lattice may be due to either the formation of stronger metal-hydrogen bonds between the titanium and tetrahedral hydrogens, although this seems unlikely, or the filling of some octahedral sites by hydrogen accompanied by the formation of an equivalent number of vacant tetrahedral sites. The contraction of the hydride lattice by the filling of octahedral sites of a fluorite-type structure has been observed among the rare earth hydrides between composition MH_2 to MH_3(15-17). The apparent dependence of lattice parameter on hydrogen pressures will be further studied in the near future.

Although the greater hydrogen pressure has the effect of decreasing the lattice parameter in the region of normal thermal expansion (Figure 9); it should be noted that the maxima of the curves have been displaced toward higher temperatures. In other words, the hydrogen pressure retards the transformation, which must occur in the hydride lattice in the region of the maxima of the curves, until the hydride lattice has expanded sufficiently. The metal-hydrogen distance for hydrogen in the tetrahedral sites never exceeds 1.93_1 Å for all temperatures and pressures. The metal-hydrogen distance at room temperature is 1.92_7 Å.

Once the conditions have been attained which favor the contraction of the lattice, then hydrogen pressure appears to have the reverse effect on the lattice parameter. The parameter å ranged from 4.459 Å at 570 psi to 4.434 Å at 15 psi. It is interesting to note that at 600°C and 15 psi hydrogen, the parameter of cubic titanium hydride is smaller than at room temperature. As previously mentioned, the parameter of cubic hafnium hydride also decreases with decreasing hydrogen pressure. The contraction of the lattice may again be atrributed to a shift of some of the hydrogen from the tetrahedral sites to the octahedral sites of the fluorite structure; however, the effect of pressure cannot be readily explained. Data from magnetic susceptibility or calorimetric studies would contribute greatly to offering an explanation for the change which occurs at the maxima of the curves (Figure 9).

Finally, the metal phase for titanium was not observed even though the hydrogen pressures were lower than those used by McQuillan in his dissociation studies (18). Some diffraction lines were observed, but could not be attributed to any definite structure. Due to the poor quality of the patterns, this phase of the study will be repeated.

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